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Feature: Fluoropolymers

Fluoropolymers for Coating Applications

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Fluorine polymers, commonly referred to as fluoropolymers, can greatly enhance the properties of coatings used in modern industrial, household and construction products. The qualities of fluoropolymer resins and oligomeric additives make them an ideal solution for applications requiring a high resistance to solvents, acids and bases, and most importantly an ability to significantly reduce friction.[1]

Such surfactant additives reduce surface energy while increasing chemical, UV, moisture, grease and dirt resistance and surface lubricity. In addition to more common fluorinated olefin-based polymers, specialty fluoroacrylates, fluorosilicone acrylates, fluorourethanes and perfluoropolyethers/ perfluoropolyoxetanes have been found to exhibit properties of interest for coatings applications.

Many of these new products are designed to address the concerns about perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) associated with many existing fluoropolymer chemistries.

Coatings containing fluorochemicals find applications in electronics (photomask covers, anti-reflection coatings), construction (highly protective coatings for exterior substrates), cool-roof coatings and optics (antifouling coatings for eyeglass lenses and liquid crystal displays). Other general coatings that may contain fluoropolymers include floor polishes, wood stains and automotive clear coats, as well as ink jet inks, pigment dispersions and adhesives.

In this article, we will review the properties of fluorochemicals and their numerous variations. We will also analyze current uses and technical applications, and how they might be utilized differently for future coatings applications.

Fluorine Atom Properties

Unique characteristics of the fluorine atom result in the interesting properties of polymers that contain them.[2] A fairly small atom, fluorine has very low polarizability and high electronegativity. Because there is a high degree of overlap between the outer orbitals of fluorine and the corresponding orbitals of second period elements, bonds formed between carbon and fluorine are very strong. The higher bond energy of the C-F bond compared to the C-H bond leads to greater thermal stability.

Perfluoropolymers, which contain only C-F bonds, have excellent chemical and weather resistance.[3] The small dipole moment of these compounds also contributes to their oil and water-repellancy, as well as their low surface tension, low refractive index, low friction coefficient and reduced adhesion to surfaces.[1]

Partially fluorinated polymers exhibit a strong electron attracting ability, resulting in a high dielectric constant and optical activity. In small molecules, this attribute leads to enhanced acidity and lipophilicity and the ability to block metabolic pathways, making fluorine-substituted compounds ideal as pharmaceuticals.[4]

Other characteristics of fluoropolymers determined by the strength of the C-F bond and the low polarizability and high electronegativity of fluorine include soil resistance, insulating properties and the ability to act as a gas barrier.[1]

PTFE and Friends – A Brief Mention

The most common commercially available fluoropolymers are based on monomers of tetrafluoroethylene, vinylidene fluoride and chlorotrifluoroethylene.[5] Both homopolymers and copolymers of these three monomers with compounds such as perfluoroalkyl vinyl ethers, hexafluoropropylene, chlorotrifluoroethylene and perfluorobutyl ethylene exhibit increased chemical and flame resistance, photo- and thermal stability and enhanced lubricity when compared to their non-fluorine containing counterparts.

These fluoropolymers find use in many applications, including chemical process equipment liners, insulating coatings for electronics, non-stick coatings for cookware, surgical patches and glass fiber fabric coatings used for roofing of large structures. Polytetrafluoroethylene (PTFE) and polyvinylidenefluouride (PVDF) are the fluoropolymers most widely used for these types of applications.

PTFE and other similar homopolymers can also be added directly to a coating formulation. In this case they function like waxes, reducing friction and increasing wear and scratch resistance.[6] With both hydrophobic and oleophobic characteristics, the fluorinated portions of the polymer tend to migrate to the surface of the coating, providing the desired properties.

While PTFE and similar products may be the most widely recognized fluoropolymers, there are significant limitations to their use in many applications. These polymers require high temperature processing and thus can only serve as coatings for temperature resistant materials. The very high crystallinity of the fluoropolymers means they are only poorly soluble in typically used organic solvents, further limiting their processability.

Incorporation of some amount of non-fluorinated monomers (ethylene or substituted derivatives, for example) into polymers prepared from fluorinated compounds like tetrafluoroethylene, chlorotrifluoroethylene or other fluorinated olefins results in copolymers with amorphous structures that retain much of the desired properties of pure fluoropolymers but exhibit improved solubilities and have lower process temperatures.[5]

Monomers containing reactive functional groups also have been found to improve the processability while adding new physical attributes.[6] These more specialized fluoropolymers have been employed as binders and/or surfactants in numerous coating applications. Fluoroacrylates have been commercially available for the longest time. Compounds receiving attention in recent years include fluorosilicone acrylates, fluorourethanes and perfluoropolyethers/perfluoropolyoxetanes.

Fluoroacrylates

Acrylic fluorinated copolymers have been used for a wide variety of applications, including anti-graffiti and easy-clean coatings[7], release coatings/liners in pressure sensitive adhesives[7], treatments for paper, paperboard and leather[8], as penetrating sealers for porous surfaces[8] and as protective coatings for electronic applications[9].

Poly(hexafluoropropylene oxide), poly(difluoromethylene oxide-co-tetrafluoroethylene oxide) and N-methyl perfluorobutanesulfonamidoethyl acrylate are examples of raw materials used for the production of fluoroacrylate polymers.[7] Fluorinated methacrylates have also been investigated for the synthesis of fluoropolymers with reduced polymerization shrinkage, improved strength and high hydrophobicity characteristics.[10]

Perfluoroalcohols containing branching perfluoroalkyl groups have been synthesized with the aim of making polyfluoroacrylates that contain perfluoro groups that extend out from the polymer backbone.[11] The fluorine content can be controlled with the size of the perfluoroalkyl groups incorporated. It is proposed that the branching structure in the fluoropolymer would form a protective outer layer and keep the polymer backbone from being exposed to harsh environments.

Fluorosilicone acrylates

Like fluoropolymers, silicone based compounds have many properties of value to coatings formulators. Hydrophobicity, wettability, leveling, mar and slip resistance and transfer resistance can all be significantly enhanced depending on the chemistry of the silicon-based resin or additive used.[6] Fluorosilicone polymers have been prepared that exhibit the advantageous characteristics of both fluorine and silicon-containing materials.

In general, polysiloxanes containing fluorinated side groups are the easiest to prepare. Acrylate-fluorosilicone alternating and block copolymers are another type. These compounds have a lower resistance to corrosive chemicals that pure fluoropolymers, but do have low surface energy and remain flexible at temperatures as low as −60°C.[12] They also can be further modified via different silicone cross-linking mechanisms.[13]

These fluoroslicone acrylates may have application in marine antifouling coatings.[6]

Fluorourethanes

Polyfluorourethanes can be produced from fluorinated diols and a traditional diisocyanate, or a fluorinated diisocynate and traditional diols. Polymers manufactured via the latter process have been shown to be nonflammable with good low temperature flexibility while providing excellent corrosion resistance.[14] The hardness can be controlled by changing the ratio of perfluorinated diisocyanate to diol.

Coatings based on some fluorourethane resins exhibit hydrophobic and super-hydrophobic properties and find applications in aircraft, marine and ground radar and microwave communication systems where they reduce rain attenuation.[15] The urethane portion of the polymer imparts the toughness, while the fluorinated groups are responsible for the very low surface energy of these coatings. Fluorinated polyurethanes have also found application as fuel storage tank linings.[16]

Perfluoropolyethers/ Perfluoropolyoxetanes

Perfluoropolyether (PFPE) compounds, which are fairly new to the coatings industry, find use as surfactants in a wide variety of formulations. These low molecular weight, partially fluorinated oxetane oligomeric polyols are non-toxic, nonflammable, chemical resistant and can be used in extreme temperatures (from -80°C to nearly 300°C).[17] They are compatible with a wide range of substrates and are recommended for use in inks and acrylic, epoxy and polyurethane coatings. In addition, unlike most traditional fluorosurfactants, PFPEs do not cause foam formation.

In PFPEs, the fluorinated groups can be found on branched side chains bound to the main polyether backbone through additional ether linkages. The length of these side chains and the degree of polymerization can be carefully controlled. The solubility of perfluoropolyoxetanes can be adjusted through copolymerization with polyepoxides.

Applications for these fluorosurfactants are numerous due to the advantageous properties they impart to coatings. These characteristics range from improving flow, wetting and leveling to increasing durability, water repellency, cleanability and chemical resistance.[18] They can be used in both waterborne, solvent based, 100% solids and UV-curable coatings, and often at levels significantly lower than higher molecular weight fluorosurfactants that have environmental fate issues.

Often perfluoropolyethers contain functional end groups that provide sites of reactivity, permitting further modification of the compounds. Examples of such chemistries include acids, alcohols, acrylates and sulfates. Modification can enable the incorporation of crosslinking mechanisms such as those necessary for UV-curing. Perfluoropolyoxetanes can also be used for the synthesis of higher molecular weight fluorochemicals that provide water repellency and stain resistance.

Overcoming the PFOA/PFOS Problem

Much research has been focused on developing alternatives to longer perfluoro chain length alcohols that can degrade to perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) and higher homologue perfluoro acids that have been shown to be biopersistant. Copolymers of fluorinated and non-fluorinated shorter chain straight and branched monomers, such as the perfluoropolyether compounds mentioned above, increase the processability while still maintaining much of the desired properties and addressing these environmental concerns.

For many years, fluoropolymers were synthesized from monomers with carbon chain lengths of eight or greater. These fluoropolymers have been shown to degrade to PFOA and/or PFOS.[19] The biopersistance of these materials has become a concern to environmental regulatory bodies around the world.

In 2006, the United States Environmental Protection Agency invited eight producers of fluoropolymers to commit to reducing both PFOA emissions and PFOA content in products. The 2010/15 PFOA Stewardship Program aims for a 95% reduction by 2010 and complete elimination by 2015.[20] All eight companies accepted the challenge, and some have already developed alternative products and are introducing them to the marketplace.

Fluorotelomers (C-6 or lower products) are not produced using PFOA and these short chain molecules cannot breakdown to PFOA in the environment. When properly designed, they exhibit similar characteristics to larger-chain fluoropolymers. These more environmentally acceptable alternatives also appear to require little change in the coating production process, helping make the transition to this newer technology go more smoothly.

Conclusion

Fluorine-rich polymers exhibit a wide range of properties that make them ideal as surfactants and binders in high performance coatings. The unique combination of chemical and thermal stability, low dielectric constant and low surface energy has led to growing interest in fluoropolymers for a wide range of applications.

Development of novel copolymers of perfluorinated alcohols, ethers, urethanes, acrylates, siloxanes and other compounds has expanded the potential scope of applications even further. Demand for cost effective, high performing, multifunctional coatings that enable materials to perform efficiently and effectively under extreme conditions with minimal environmental impact (energy consumption, VOC emissions, toxicity, carbon footprint, etc.) continues to increase. These specialty fluoropolymers possess many characteristics that make them ideally suited for use in such novel coating formulations.

Recognition of the environmental issues surrounding higher chain length fluoropolymers has led producers to increase research efforts for the identification of short chain alternatives that provide similar performance characteristics. These efforts will result in the development of additional new fluorochemicals and ensure the continued growth of the fluoropolymer market.

Note on the author: Barry Jones serves as the Technical Director at Halocarbon Products Corporation, where he puts to use decades of experience leading the development of new specialty fluorochemicals and

the scale up of their production. He has a Bachelors degree in chemical engineering from the University of Bradford in the UK.

Halocarbon is a leading producer of specialty fluorochemicals, manufacturing inert oils, greases and waxes, aliphatic fluorochemicals, inhalation anesthetics and other more. Fluorinated alcohols, diols, allyls, vinyls, butynes and amines from Halocarbon can be used to produce resins that exhibit unique properties when incorporated into coating formulations. The company also welcomes the opportunity to develop custom synthesis routes to novel fluorochemicals.

Beneficial Properties of Fluoropolymers for Coating Formulations

- Low surface energy
- Chemical and moisture resistance
- Oil and grease resistance
- Adhesion to low energy surfaces
- Low refractive index
- Surface lubricity
- Soil/dirt resistance
- Heat resistance
- Abrasion resistance
- Vapor permeability
- UV resistance
- Non-stick characteristics
- Excellent electrical insulation and dielectric properties

Possible Characteristics of Coatings Containing Fluoropolymers

- Improved weatherability
- Improved wettability
- Improved corrosion resistance
- Improved stain resistance
- Easy to clean
- Enhanced durability/stability in extreme environments
- Improved flow, leveling, adhesion, gloss, clarity, etc.
- Smoother finishes (reduction of surface blemishes)
- Enhanced release properties
- Enhanced anti-static properties.

- Fire-retardancy

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